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**THIS NASA INVENTION APPEARS TO HAVE  
EXCELLENT COMMERCIAL POTENTIAL**

NASA CASE NO. **LEW-13,556-1**

PRINT FIG. **1**

**NOTICE**

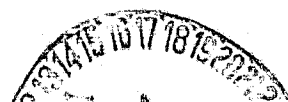
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(NASA-Case-LEW-13556-1) POLYVINYL ALCOHOL  
BATTERY SEPARATOR CONTAINING INERT FILLER  
Patent Application (NASA) 14 p  
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LEW

POLYVINYL ALCOHOL  
BATTERY SEPARATOR  
CONTAINING INERT FILLER

AWARDS ABSTRACT

A battery separator for an alkaline battery is disclosed which has enhanced performance and increased cycle life. In a particular example, the number of cycles that can be attained before the onset of capacity loss when using the present battery separator increases 4-5 times when compared with a conventional separator. These results are achieved by incorporating any one of several readily available and inexpensive filler materials in an otherwise conventional type of battery separator. Conventional techniques and equipment used previously to manufacture the battery separator may be employed.

The battery separator is made up of cross-linked polyvinyl alcohol having dispersed therein fine particles of a filler material which is inert with respect to the alkaline electrolyte of an alkaline battery. The filler is present in an amount of from 1 to 20% by weight of the polyvinyl alcohol and has a particle size of up to 50 microns. The new separator is produced in the same way in which cross-linked battery separators may be made except that the particulate filler is intimately admixed with the polyvinyl alcohol prior to shaping and cross-linking the product. Suitable fillers include titania and silicates and many other readily available materials.

Novelty appears to reside in the incorporation of this amount of filler in a cross-linked polyvinyl alcohol battery separator and in achieving enhanced battery performance by the use of the filler.

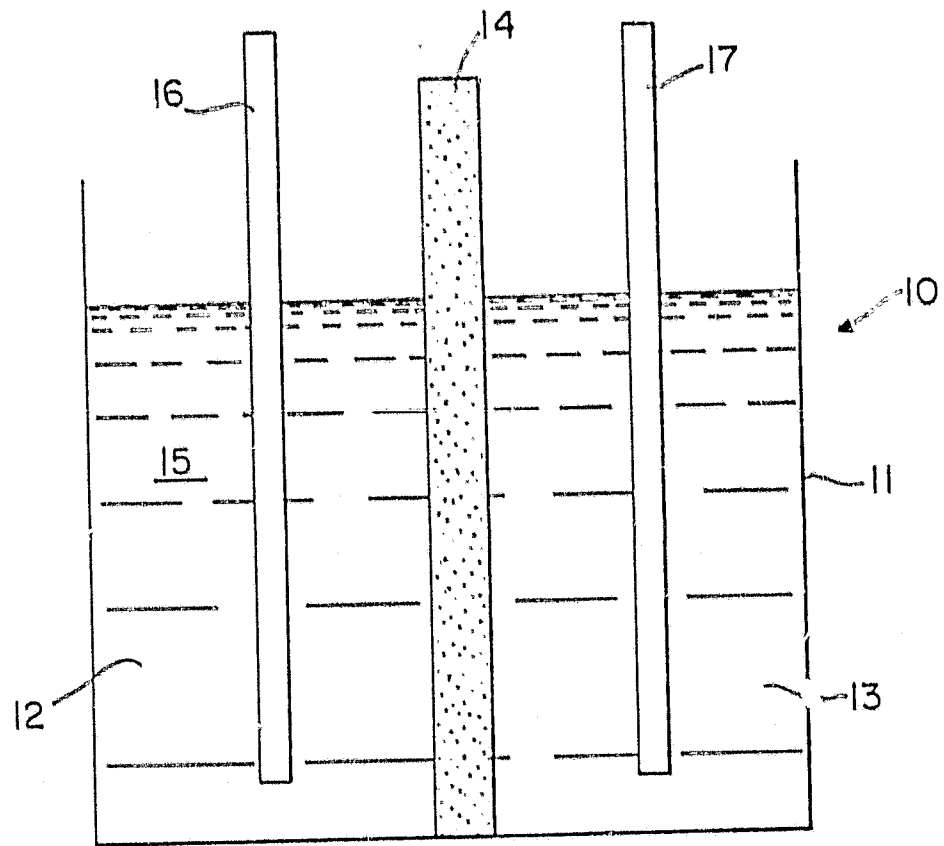
Inventors: Dean W. Sheibley  
Li-Chen Hsu  
Michelle A. Manzo

Employer: NASA Lewis Research Center

Evaluator: J. Stuart Fordyce

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- 1 -

POLYVINYL ALCOHOL BATTERY  
SEPARATOR CONTAINING INERT FILLER

Origin of the Invention

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

Background of the Invention

10 This invention relates to alkaline batteries. More particularly, the invention relates to separators for alkaline batteries. Still more particularly, the invention relates to such separators which comprise cross-linked polyvinyl alcohol.

15 Alkaline batteries are well known and are described in considerable detail in the literature, including U.S. Patent No. 2,635,127 of Yardney et al; U.S. Patent No. 2,648,717 of Ross et al; U.S. Patent No. 3,269,869 of Mendelsohn; and U.S. Patent No. 4,157,423 of Gaddesaud,

20 the disclosure of each of which is incorporated herein by reference.

One of the key items of an alkaline battery is the separator, a membrane which is interposed between the electrodes of the battery and which is in contact

25 with the alkaline electrolyte. Battery separators are discussed at some length in the foregoing patents and elsewhere, including the following patents: U.S. Patent 4,085,241 of Sheibley; U.S. Patent 4,154,912 of Philip et al; and U.S. Patent 4,224,393 of Fienberg et al, the

30 disclosure of each of which is incorporated herein by reference.

One type of battery separator which has received considerable attention, and which is referred to in sev-

eral of the foregoing patents, comprises cross-linked polyvinyl alcohol. These separators are typically made by casting an aqueous solution containing 5-20% by weight of film-forming polyvinyl alcohol into a film, and drying and cross-linking the film. Cross-linking may be achieved in any of several ways, such as by treatment of a polyvinyl alcohol film with an acid solution of an aldehyde cross-linking agent. Suitable methods include those disclosed in U.S. Patent 4,157,423 of Gaddesaud; U.S. Application Ser. No. 145,271, now U.S. Patent No. of Hsu et al; and U.S. application No. 113,014, now U.S. Patent No. of Philipp et al, the disclosure of each of which is incorporated herein by reference.

While the cross-linked polyvinyl alcohol battery separators know heretofore have proven to be satisfactory, there is a continuing need for improvement, particularly in battery performance. It is an object of the present invention to provide a battery separator which enhances alkaline battery performance and to provide alkaline batteries with enhanced performance.

#### Brief Summary of the Invention

The foregoing and other objects which will be apparent to those of ordinary skill in the art are achieved in accordance with the present invention by providing a battery separator for an alkaline battery comprising a water-insoluble cross-linked polyvinyl alcohol film having a thickness of not more than 20 mils, and a particulate, electrolyte-inert filler dispersed throughout said film, said filler being present in an amount of from 1 to 20% by weight based on the weight of the polyvinyl alcohol and having a particle size of up to 50 microns, and by providing an alkaline battery comprising an alkaline electrolyte, a positive electrode, a negative electrode, and a battery separator as just described.

It is appropriate to point out here that the use of at least some of the present filler materials in battery separators or in combination with polyvinyl alcohol films is not new. For example, Miller et al, U.S. Patent 3,256,536 discloses a film of polyvinyl alcohol containing a large amount of a filler material for use in a fuel cell. The present invention employs a generally low amount of filler since a higher amount results in a brittle film which is not useful. Several patents, such as Watanabe, U.S. Patent No. 3,647,552, disclose soluble (non cross-linked) polyvinyl alcohol films in dry cells, which contain e.g. silica. Silica, however, is not useful in the present invention because of its lack of inertness in alkaline electrolyte. Moreover, some of the filler materials of the present invention have been used in other battery separators. For example, Afrance et al, U.S. Patent No. 3,861,963 discloses a battery separator made up of a relatively large amount of ceramic fiber and potassium based fibers and a relatively small amount of rubber based binder. Sheibley, U.S. Patent No. 4,085,241, discloses the use of unreactive and reactive fillers in a battery separator made up of a rubber-based resin copolymer.

#### Brief Description of the Drawing

There follows a detailed description of preferred embodiments of the invention including the drawing in which:  
the sole figure is a diagrammatic side elevation view of an alkaline battery incorporating a battery separator according to the invention.

#### Description of Preferred Embodiments

The drawing illustrates, in a diagrammatic manner, the basic elements of an alkaline battery 10. A casing 11 is divided into a positive electrode chamber 12 and a negative electrode chamber 13 by a battery separator 14 in accordance with the invention. An alkaline electrolyte 15, such as potassium hydroxide, is provided within

casing 11. A positive electrode 16, typically comprising silver oxide, is supported, by means not shown, in compartment 12, and a negative electrode 17, typically comprising zinc, is similarly supported in compartment 13. Suitable electrical leads are connectable to the electrodes for connection to an external electrical circuit. As mentioned above, the structural and operational details of the alkaline battery are well known and will not be described here.

10       The following examples illustrate the invention.

Example 1

A solution mixture for casting a film is made from:

|    | <u>Ingredient</u>   | <u>Parts by Weight</u> |
|----|---|------------------------|
|    | Medium Viscosity Polyvinyl Alcohol (PVA)                      | 250                    |
| 15 | (10% Solution in Water)                                       |                        |
|    | Wetting Agent (4 grams Triton X-100/500 ml Water)             | 0.5                    |
|    | Calcium Zirconium Silicate 9CZS, TAM Products, NL Industries) | 1.09                   |
|    | Titanium Dioxide (Degussa P-25)                               | .19                    |
| 20 | Water   | 50.0                   |

The ingredients are mixed well in a high-shear mixer or blender and then heated to 120°F-140°F. The mixture is then placed in a vacuum chamber and the air bubbles removed by deaeration. The mixture is then cast at a wet thickness of 50 to 60 mil to provide a dry film of 2-5 mils. The film is allowed to dry at room temperature overnight. It can also be dried with heat.

The dry film is then immersed in a solution consisting of 1000 ml water, 20 grams  $KIO_4$ , 20 ml of concentrated sulfuric acid, and 200 grams of sodium sulfate. The solution is heated from room temperature to 75-90°C and held at that temperature for 15 minutes. The film should be cross-linked. (If the film is cross-linked, it will not dissolve when immersed in boiling water for more than 5 minutes.) The film is removed from the



cross-linking solution and rinsed several times with water to remove traces of acid and sodium sulfate.

### Example 2

A solution mixture for casting is made from:

|    | <u>Ingredient</u>  | <u>Parts by Weight</u> |
|----|--|------------------------|
| 5  | Medium viscosity PVA (10% solution)  | 500                    |
|    | Wetting Agent (4 grams Triton X-100/500 ml water)  | 0.5                    |
|    | Dialdehyde of Furan (DAF)  | 1                      |
|    | Hydrated Clay  | 0.7                    |
| 10 | Unitar 110 (Titania)   | 0.96                   |
|    | P-25 (Titania)   | 0.43                   |
|    | Lead zirconate-Titanate  | 0.41                   |
|    | Water  | 50                     |
|    | Tamol (2% solution in water) dispersing agent  | .4                     |
| 15 | The mixture of clay, titania, and lead zirconate-titanate, water and dispersing agent are premixed, then added to the solution of PVA, DAF and wetting agent. The mixture is mixed well in a high shear mixer or blender, heated to 120-140°F, then deaerated to remove air bubbles. It is cast at 35 mils wet to obtain a dry film ranging from 2-5 mils, after overnight drying. The dry film is then immersed in a solution consisting of 1000 ml H <sub>2</sub> O, 100 grams Na <sub>2</sub> SO <sub>4</sub> and 20 ml concentrated H <sub>2</sub> SO <sub>4</sub> , heated to 75°C to 90°C and held there for 15 minutes. |                        |
| 20 |  |                        |
| 25 | The film is then removed from the solution and rinsed several times in water to remove the residual acid and sodium sulfate.   |                        |

### Example 3

A solution mixture for casting is made from:

|    | <u>Ingredient</u>                                 | <u>Parts by Weight</u> |
|----|---|------------------------|
| 30 | Medium viscosity PVA (10% solution)               | 500                    |
|    | Wetting Agent (4 grams Triton X-100/500 ml water) | 0.5                    |
|    | Dialdehyde of Starch                              | 1                      |
|    | 200 mesh white pine wood flour                    | 5                      |
| 35 | Water   | 50                     |

The mixing procedure is the same as Example 1.

The dry film is cross-linked by the methods of either Example 1 or Example 2.

The advantage of the use of fillers has been demonstrated in several Ni/Zn cell tests; these tests show that the number of cycles attained to the onset of loss of capacity increase from 4 to 5 times when about 5% by weight filler is added to PVA and then periodate or acid cross-linked. Cycle life data in amp-hr Ni/Zn cells at 50% depth of discharge (DOD) shows that the onset of capacity loss occurs at 50 cycles for periodate cross-linked medium viscosity PVA with no fillers. With 5% filler content, the onset of capacity loss extends to 280 cycles. Similarly, the addition of 5% filler to an acid catalyzed, dialdehyde cross-linked PVA film extends the cycles from 40 to 222. Also, performance characterization in Ni/Zn cells shows that load voltages at different discharge rates are higher, and better cell capacity is attained from cross-linked PVA film with fillers than film without fillers. Table 1 shows results of separator evaluation tests on three periodate cross-linked films: no filler; with filler; and with filler plus dialdehyde cross-linker. The resistivity improves significantly with the addition of fillers as does the zinc dendrite penetration rate. Zincate diffusivity value improves somewhat with filler addition only.

TABLE I

COMPARISON OF VOLUME RESISTIVITY, ZINC DENDRITE PENETRATION RATE AND ZINCATE DIFFUSIVITY OF PERIodate CROSS-LINKED PVA WITH FILLERS AND FILLER PLUS DIALDEHYDE

| 5  | FILM TYPE    | VOL. RES. | ZN DENDR.            | ZINCATE DIFF.               |
|----|--------------|-----------|----------------------|-----------------------------|
|    |              | OHM-CM    | CM/MIN               | MOLES/CM <sup>2</sup> -MIN. |
|    | Periodate-   |           |                      |                             |
|    | no filler    | 204       | $2.2 \times 10^{-4}$ | $1.7 \times 10^{-8}$        |
|    | Periodate-   |           |                      |                             |
| 10 | 5% filler(s) | 30        | $9.6 \times 10^{-5}$ | $1.1 \times 10^{-8}$        |
|    | Periodate-   |           |                      |                             |
|    | 2% DAF-5%    |           |                      |                             |
|    | filler(s)    | 30        | $8.2 \times 10^{-5}$ | $1.7 \times 10^{-7}$        |

Addition of fillers above 20% by weight based on weight of PVA results in dry films which are brittle and subject to cracking when handled. The preferred method of making the film is to make a PVA dialdehyde blend with the dialdehyde content between 2 and 10% of the amount required to theoretically cross-link the PVA hydroxyl groups present (the preferred amount being 2 to 5%) and about 5% filler(s) based on the weight of PVA. Cross-linking is effected by treatment of the film with an acid solution. The dry film thickness of two mils is preferred since this permits multiple wraps around the electrodes without significantly increasing the amount of separation between the electrodes when used with an absorber. In general, film thickness is not greater than about 20 mils and preferably about 1-5 mils.

The polyvinyl alcohol resin useful in the invention is a conventional, film-forming, polymeric material readily available commercially and can be of the type used heretofore for making separators for alkaline batteries. Commercially available polyvinyl alcohol normally contains about 0.5 to 6% of 1,2-diol units in the predominantly 1,3-diol structure. The presence of 1,2-

diol units in the chain results in reduced resistance to oxidation. Accordingly, it is preferred, in the practice of the present invention, to use a polyvinyl alcohol substantially free (i.e. containing less than about 5%) of 1,2-diol units. Polyvinyl alcohol having an essentially head-to-tail structure of this type is readily available. It is made by the alcoholysis of polyvinyl acetate having an essentially head-to-tail structure which is made by low temperature polymerization of vinyl acetate. The polyvinyl alcohol is a film-forming resin having, generally, a number average molecular weight of 10,000-200,000 and is conveniently provided and used in aqueous solution such as 10-20% resin by weight. The amount of PVA used in the present process is generally from 3 to 20% by weight, based on the total amount of PVA and water in the aqueous admixture. Preferably, the amount of PVA is from 5-15%, same basis.

The fillers useful in the invention may vary considerably but must be insoluble in and not reactive with the alkaline battery electrolyte. However, materials which react very slowly with the electrolyte - such as calcium silicate - are useful since the rate of reaction is very slow compared with the life of the battery. Similarly, included in the term "insoluble" are fillers that are very sparingly soluble in the electrolyte.

The filler is preferably made up of two or more fractions of different particle size. A preferred filler is made up of those fractions having the following size ranges (in terms of square meters of surface area per gram):

Fraction 1: greater than 25  $M^2$ /gram

Fraction 2: 10-25  $M^2$ /gr.

Fraction 3: 10  $M^2$ /gr.

Preferably, the particle sizes in the first group do not exceed 250  $M^2$ /gr. Use of these three ranges of

particle sizes can result in mean particle diameters which are less than or equal to 1/8 the mean diameter of the next larger group: 0.01 to 0.02 microns, 0.1 to 0.2 microns, and 1 to 3 microns. The two basic particle size ranges which are used to control resistivity of the battery separator in the present invention are groups 1 and 2 above (greater than 25  $M^2$  per gram and 10-25  $M^2$  per gram). Preferably, the filler particles in this basic combination are restricted in size to the 0.01 to 0.2 micron range (10  $M^2$  per gram to 250  $M^2$  per gram). To this base combination, inert fillers falling within the third particle size group (less than 10  $M^2$  per gram) can be added. Preferably, the third group of filler particles (less than 10  $M^2$ /gram) should not have a particle diameter greater than about 20 microns.

The filler particles which fall within the group 1 range (greater than 25  $M^2$ /gram) represent 5 to 15% by weight of the total filler weight. The second group of particles (10 to 25  $M^2$ /gram) represent from 60 to 95% by weight of the total filler weight. The third group of filler particles (less than 10  $M^2$ /gram) represent from 0 to 23% by weight, preferably 5 to 15% by weight, each based upon the total filler weight.

The filler materials used in each of the three groups may be the same or different and mixtures of filler materials may be used within each group.

Useful fillers include widely different materials such as clays, wood flour, and lignin. Suitable fillers include: clays, titanates, zirconates, oxides, silicates, naturally occurring fibrous materials such as cotton flock, wood flour, and lignin. Among suitable clays are kaolin and kaolinites, saponite and hectorite. Among suitable titanates are alkali metal titanates such as potassium titanate, alkaline earth metal titanates such as calcium and magnesium titanates. Other suitable

titanates include lead titanate, nickel titanate, zirconium titanate, lead zirconium titanate, lead zirconate titanate, and zinc magnesium titanate. Suitable zirconates include alkaline earth metal zirconates such as magnesium zirconate and others such as lead zirconate-titanate. Suitable oxides include titania and zirconia. Suitable silicates include alumina, magnesium, zinc, calcium, and iron silicate, aluminosilicates such as magnesium aluminum silicate, and others such as calcium zirconium silicate, magnesium zirconium silicate and zinc zirconium silicate. A suitable wood flour is minus 200 mesh white pine wood flour. A suitable lignin is from the Kraft process.

Where three fractions of filler particles are used as described above, the preferred filler materials for the first fraction of filler particles (surface area greater than  $25 \text{ M}^2/\text{gram}$ ) are titania, synthetic hectorite, and saponite. The preferred filler materials for the second fraction (surface areas of  $10 \text{ M}^2/\text{gram}$  to  $25 \text{ M}^2/\text{gram}$ ) are fine-particle clays, such as kaolin, and titania. The preferred filler materials for the third fraction of filler particles (surface areas less than  $10 \text{ M}^2/\text{gram}$ ) are titanates, such as potassium titanate and lead titanate, zirconates, oxides, such as calcium-stabilized zirconium oxide, wood flour, lignin, natural and synthetic silicates such as magnesium silicate, zinc silicate, iron silicate, and aluminosilicates, cotton flock, and naturally occurring fibrous materials. The most preferred fillers in order of most preferred to least preferred are lead zirconate-titanate, lead titanate, calcium zirconium silicate, and wood flour (200 mesh).

POLYVINYL ALCOHOL  
BATTERY SEPARATOR  
CONTAINING INERT FILLER

Abstract of the Disclosure

5       A cross-linked polyvinyl alcohol battery separator.  
A particulate filler, inert to alkaline electrolyte of  
an alkaline battery, is incorporated in the separator in an  
amount of 1-20% by weight, based on the weight of the  
polyvinyl alcohol, and is dispersed throughout the pro-  
10 duct. Incorporation of the filler enhances performance  
and increases cycle life of alkaline batteries when com-  
pared with batteries containing a similar separator not  
containing filler. Suitable fillers include titanates,  
silicates, zirconates, aluminates, wood flour, lignin,  
15 and titania. Particle size is not greater than about  
50 microns.